

CLAIMS

1. An electrically conductive paste for connecting thermoelectric materials comprising:

5 (i) at least one powdery oxide selected from the group consisting of complex oxides (a) to (d):

10 (a) a complex oxide represented by the formula $Ca_aA^{1b}Co_cA^{2d}O_e$ wherein A^1 is one or more elements selected from the group consisting of Na, K, Li, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Pb, Sr, Ba, Al, Bi, Y, and lanthanoids; A^2 is one or more elements selected from the group consisting of Ti, V, Cr, Mn, Fe, Ni, Cu, Mo, W, Nb, and Ta; $2.2 \leq a \leq 3.6$; $0 \leq b \leq 0.8$; $2 \leq c \leq 4.5$; $0 \leq d \leq 2$; and $8 \leq e \leq 10$;

15 (b) a complex oxide represented by the formula $BifPb_gM^{1h}Co_iM^{2j}O_k$ wherein M^1 is one or more elements selected from the group consisting of Na, K, Li, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Pb, Ca, Sr, Ba, Al, Y, and lanthanoids; M^2 is one or more elements selected from the group consisting of Ti, V, Cr, Mn, Fe, Ni, Cu, Mo, W, Nb, and Ta; $1.8 \leq f \leq 2.2$; $0 \leq g \leq 0.4$; $1.8 \leq h \leq 2.2$; $1.6 \leq i \leq 2.2$; $0 \leq j \leq 0.5$; and $8 \leq k \leq 10$;

20 (c) a complex oxide represented by the formula $Ln_mR^{1n}Ni_pR^{2q}O_r$ wherein Ln is one or more elements selected from the group consisting of lanthanoids; R^1 is one or more elements selected from the group consisting of Na, K, Sr, Ca, and Bi; R^2 is one or more elements selected from the group consisting of Ti, V, Cr, Mn, Fe, Ni, Cu, Mo, W, Nb, and Ta; $0.5 \leq m \leq 1.2$; $0 \leq n \leq 0.5$; $0.5 \leq p \leq 1.2$; $0 \leq q \leq 0.5$; and $2.7 \leq r \leq 3.3$;

25 (d) a complex oxide represented by the formula $(Ln_sR^{3t})_2Ni_uR^{4v}O_w$ wherein Ln is one or more elements selected from the group consisting of lanthanoids; R^3 is one or more elements selected from the group consisting of Na, K, Sr, Ca, and Bi; R^4 is one or more elements selected from the group consisting of Ti, V, Cr, Mn, Fe, Ni, Cu, Mo, W, Nb, and Ta; $0.5 \leq s \leq 1.2$; $0 \leq t \leq 0.5$; $0.5 \leq u \leq 1.2$; $0 \leq v \leq 0.5$; and $3.6 \leq r \leq 4.4$; and

30 (ii) at least one powdery electrically conductive metal selected from the group consisting of gold, silver, platinum, and alloys containing

at least one of these metals.

2. The electrically conductive paste for connecting thermoelectric materials according to Claim 1, wherein the powdery oxide mentioned 5 in (i) above is contained in an amount of 0.5 to 20 parts by weight per 100 parts by weight of the powdery electrically conductive metal mentioned in (ii) above.

3. The electrically conductive paste for connecting thermoelectric 10 materials according to Claim 1, further comprising a glass ingredient and a resin ingredient.

4. An electrically conductive paste for connecting a p-type thermoelectric material comprising:

15 (i) at least one powdery oxide selected from the group consisting of:
a complex oxide represented by the formula $Ca_aA^{1b}Co_cA^{2d}O_e$ wherein A^1 is one or more elements selected from the group consisting of Na, K, Li, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Pb, Sr, Ba, Al, Bi, Y, and lanthanoids; A^2 is one or more elements selected from the group 20 consisting of Ti, V, Cr, Mn, Fe, Ni, Cu, Mo, W, Nb, and Ta; $2.2 \leq a \leq 3.6$; $0 \leq b \leq 0.8$; $2 \leq c \leq 4.5$; $0 \leq d \leq 2$; and $8 \leq e \leq 10$; and
a complex oxide represented by the formula $BifPb_gM^{1h}Co_iM^{2j}O_k$ wherein M^1 is one or more elements selected from the group consisting of Na, K, Li, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Pb, Ca, Sr, Ba, Al, Y, 25 and lanthanoids; M^2 is one or more elements selected from the group consisting of Ti, V, Cr, Mn, Fe, Ni, Cu, Mo, W, Nb, and Ta; $1.8 \leq f \leq 2.2$; $0 \leq g \leq 0.4$; $1.8 \leq h \leq 2.2$; $1.6 \leq i \leq 2.2$; $0 \leq j \leq 0.5$; and $8 \leq k \leq 10$; and
(ii) at least one powdery electrically conductive metal selected from 30 the group consisting of gold, silver, platinum, and alloys containing at least one of these metals.

5. The electrically conductive paste for connecting a p-type thermoelectric material according to Claim 4, wherein the powdery oxide 35 is at least one member selected from the group consisting of:

a complex oxide represented by the formula $\text{Ca}_a\text{A}^1\text{bCo}_4\text{O}_e$ wherein A^1 is one or more elements selected from the group consisting of Na, K, Li, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Pb, Sr, Ba, Al, Bi, Y, and lanthanoids; $2.2 \leq a \leq 3.6$; $0 \leq b \leq 0.8$; and $8 \leq e \leq 10$; and

5 a complex oxide represented by the formula $\text{Bi}_f\text{Pb}_g\text{M}^1\text{hCo}_2\text{O}_k$ wherein M^1 is one or more elements selected from the group consisting of Sr, Ca, and Ba; $1.8 \leq f \leq 2.2$; $0 \leq g \leq 0.4$; $1.8 \leq h \leq 2.2$; and $8 \leq k \leq 10$.

10 6. The electrically conductive paste for connecting a p-type thermoelectric material according to Claim 4, wherein the powdery oxide mentioned in (i) above is contained in an amount of 0.5 to 20 parts by weight per 100 parts by weight of the powdery electrically conductive metal mentioned in (ii) above.

15 7. The electrically conductive paste for connecting a p-type thermoelectric material according to Claim 4, further comprising a glass ingredient and a resin ingredient.

20 8. An electrically conductive paste for connecting an n-type thermoelectric material comprising:

(i) at least one powdery oxide selected from the group consisting of:
a complex oxide represented by the formula $\text{Ln}_m\text{R}^1\text{nNi}_p\text{R}^2\text{qO}_r$ wherein Ln is one or more elements selected from the group consisting of lanthanoids; R^1 is one or more elements selected from the group consisting of Na, K, Sr, Ca, and Bi; R^2 is one or more elements selected from the group consisting of Ti, V, Cr, Mn, Fe, Ni, Cu, Mo, W, Nb, and Ta; $0.5 \leq m \leq 1.2$; $0 \leq n \leq 0.5$; $0.5 \leq p \leq 1.2$; $0 \leq q \leq 0.5$; and $2.7 \leq r \leq 3.3$; and

30 a complex oxide represented by the formula $(\text{Ln}_s\text{R}^3\text{t})_2\text{Ni}_u\text{R}^4\text{vO}_w$ wherein Ln is one or more elements selected from the group consisting of lanthanoids; R^3 is one or more elements selected from the group consisting of Na, K, Sr, Ca, and Bi; R^4 is one or more elements selected from the group consisting of Ti, V, Cr, Mn, Fe, Ni, Cu, Mo, W, Nb, and Ta; $0.5 \leq s \leq 1.2$; $0 \leq t \leq 0.5$; $0.5 \leq u \leq 1.2$; $0 \leq v \leq 0.5$; and

3.6 ≤ r ≤ 4.4; and

(ii) at least one powdery electrically conductive metal selected from the group consisting of gold, silver, platinum, and alloys containing at least one of these metals.

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9. The electrically conductive paste for connecting an n-type thermoelectric material according to Claim 8, wherein the powdery oxide is at least one member selected from the group consisting of:

a complex oxide represented by the formula $La_mR^1_nNiO_r$ wherein

10 R^1 is one or more elements selected from the group consisting of Na, K, Sr, Ca, and Bi; $0.5 \leq m \leq 1.2$; $0 \leq n \leq 0.5$; and $2.7 \leq r \leq 3.3$; and

a complex oxide represented by the formula $(La_sR^3_t)_2NiO_w$

wherein R^3 is one or more elements selected from the group consisting of Na, K, Sr, Ca, and Bi; $0.5 \leq s \leq 1.2$; $0 \leq t \leq 0.5$; and $3.6 \leq w \leq$

15 4.4.

10. The electrically conductive paste for connecting an n-type thermoelectric material according to Claim 8, wherein the powdery oxide mentioned in (i) above is contained in an amount of 0.5 to 20 parts
20 by weight per 100 parts by weight of the powdery electrically conductive metal mentioned in (ii) above.

11. The electrically conductive paste for connecting an n-type thermoelectric material according to Claim 8, further comprising a
25 glass ingredient and a resin ingredient.

12. A thermoelectric element wherein one end of a p-type thermoelectric material and one end of an n-type thermoelectric material are each connected to an electrically conductive substrate with an electrically
30 conductive paste,

the p-type thermoelectric material comprising:

a complex oxide represented by the formula $Ca_aA^1_bCo_cA^2_dO_e$
wherein A^1 is one or more elements selected from the group consisting
35 of Na, K, Li, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Pb, Sr, Ba, Al, Bi, Y,
and lanthanoids; A^2 is one or more elements selected from the group

consisting of Ti, V, Cr, Mn, Fe, Ni, Cu, Mo, W, Nb, and Ta; $2.2 \leq a \leq 3.6$; $0 \leq b \leq 0.8$; $2 \leq c \leq 4.5$; $0 \leq d \leq 2$; and $8 \leq e \leq 10$; or

a complex oxide represented by the formula $Bi_f Pb_g M^1_h Co_i M^2_j O_k$ wherein M^1 is one or more elements selected from the group consisting of Na, K, Li, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Pb, Ca, Sr, Ba, Al, Y, and lanthanoids; M^2 is one or more elements selected from the group consisting of Ti, V, Cr, Mn, Fe, Ni, Cu, Mo, W, Nb, and Ta; $1.8 \leq f \leq 2.2$; $0 \leq g \leq 0.4$; $1.8 \leq h \leq 2.2$; $1.6 \leq i \leq 2.2$; $0 \leq j \leq 0.5$; and $8 \leq k \leq 10$;

10 the n-type thermoelectric material comprising:

a complex oxide represented by the formula $Ln_m R^1_n Ni_p R^2_q O_r$ wherein Ln is one or more elements selected from the group consisting of lanthanoids; R^1 is one or more elements selected from the group consisting of Na, K, Sr, Ca, and Bi; R^2 is one or more elements selected from the group consisting of Ti, V, Cr, Mn, Fe, Ni, Cu, Mo, W, Nb, and Ta; $0.5 \leq m \leq 1.2$; $0 \leq n \leq 0.5$; $0.5 \leq p \leq 1.2$; $0 \leq q \leq 0.5$; and $2.7 \leq r \leq 3.3$; or

a complex oxide represented by the formula $(Ln_s R^3_t)_2 Ni_u R^4_v O_w$ wherein Ln is one or more elements selected from the group consisting of lanthanoids; R^3 is one or more elements selected from the group consisting of Na, K, Sr, Ca, and Bi; R^4 is one or more elements selected from the group consisting of Ti, V, Cr, Mn, Fe, Ni, Cu, Mo, W, Nb, and Ta; $0.5 \leq s \leq 1.2$; $0 \leq t \leq 0.5$; $0.5 \leq u \leq 1.2$; $0 \leq v \leq 0.5$; and $3.6 \leq r \leq 4.4$; and

25 the p-type thermoelectric material and the n-type thermoelectric material being each connected to the electrically conductive substrate with the electrically conductive paste of claim 1.

30 13. A thermoelectric element wherein one end of a p-type thermoelectric material and one end of an n-type thermoelectric material are each connected to an electrically conductive substrate with an electrically conductive paste,

the p-type thermoelectric material comprising:

35 a complex oxide represented by the formula $Ca_a A^1_b Co_c A^2_d O_e$

wherein A^1 is one or more elements selected from the group consisting of Na, K, Li, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Pb, Sr, Ba, Al, Bi, Y, and lanthanoids; A^2 is one or more elements selected from the group consisting of Ti, V, Cr, Mn, Fe, Ni, Cu, Mo, W, Nb, and Ta; $2.2 \leq a \leq 3.6$; $0 \leq b \leq 0.8$; $2 \leq c \leq 4.5$; $0 \leq d \leq 2$; and $8 \leq e \leq 10$; or

5 a complex oxide represented by the formula $BifPb_gM^1hCo_iM^2jO_k$ wherein M^1 is one or more elements selected from the group consisting of Na, K, Li, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Pb, Ca, Sr, Ba, Al, Y, and lanthanoids; M^2 is one or more elements selected from the group 10 consisting of Ti, V, Cr, Mn, Fe, Ni, Cu, Mo, W, Nb, and Ta; $1.8 \leq f \leq 2.2$; $0 \leq g \leq 0.4$; $1.8 \leq h \leq 2.2$; $1.6 \leq i \leq 2.2$; $0 \leq j \leq 0.5$; and $8 \leq k \leq 10$;

the n-type thermoelectric material comprising:

a complex oxide represented by the formula $Ln_mR^1nNi_pR^2qO_r$

15 wherein Ln is one or more elements selected from the group consisting of lanthanoids; R^1 is one or more elements selected from the group consisting of Na, K, Sr, Ca, and Bi; R^2 is one or more elements selected from the group consisting of Ti, V, Cr, Mn, Fe, Ni, Cu, Mo, W, Nb, and Ta; $0.5 \leq m \leq 1.2$; $0 \leq n \leq 0.5$; $0.5 \leq p \leq 1.2$; $0 \leq q \leq 0.5$; and 20 $2.7 \leq r \leq 3.3$; or

a complex oxide represented by the formula $(Ln_sR^3t)_2Ni_uR^4vO_w$ wherein Ln is one or more elements selected from the group consisting of lanthanoids; R^3 is one or more elements selected from the group consisting of Na, K, Sr, Ca, and Bi; R^4 is one or more elements selected 25 from the group consisting of Ti, V, Cr, Mn, Fe, Ni, Cu, Mo, W, Nb, and Ta; $0.5 \leq s \leq 1.2$; $0 \leq t \leq 0.5$; $0.5 \leq u \leq 1.2$; $0 \leq v \leq 0.5$; and $3.6 \leq r \leq 4.4$;

the electrically conductive paste for connecting the p-type thermoelectric material comprising:

30 (i) at least one powdery oxide selected from the group consisting of a complex oxide represented by the formula $Ca_aA^1bCo_cA^2dO_e$ wherein A^1 is one or more elements selected from the group consisting of Na, K, Li, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Pb, Sr, Ba, Al, Bi, Y, and lanthanoids; A^2 is one or more elements selected from the group 35 consisting of Ti, V, Cr, Mn, Fe, Ni, Cu, Mo, W, Nb, and Ta; $2.2 \leq a$

≤ 3.6 ; $0 \leq b \leq 0.8$; $2 \leq c \leq 4.5$; $0 \leq d \leq 2$; and $8 \leq e \leq 10$; and a complex oxide represented by the formula $\text{Bi}_f\text{Pb}_g\text{M}^1_h\text{Co}_i\text{M}^2_j\text{O}_k$ wherein M^1 is one or more elements selected from the group consisting of Na, K, Li, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Pb, Ca, Sr, Ba, Al, Y, and lanthanoids; M^2 is one or more elements selected from the group consisting of Ti, V, Cr, Mn, Fe, Ni, Cu, Mo, W, Nb, and Ta; $1.8 \leq f \leq 2.2$; $0 \leq g \leq 0.4$; $1.8 \leq h \leq 2.2$; $1.6 \leq i \leq 2.2$; $0 \leq j \leq 0.5$; and $8 \leq k \leq 10$; and

10 (ii) at least one powdery electrically conductive metal selected from the group consisting of gold, silver, platinum, and alloys containing at least one of these metals; and

the electrically conductive paste for connecting the n-type thermoelectric material comprising:
 15 (i) at least one powdery oxide selected from the group consisting of a complex oxide represented by the formula $\text{Ln}_m\text{R}^1_n\text{Ni}_p\text{R}^2_q\text{O}_r$ wherein Ln is one or more elements selected from the group consisting of lanthanoids; R^1 is one or more elements selected from the group consisting of Na, K, Sr, Ca, and Bi; R^2 is one or more elements selected from the group consisting of Ti, V, Cr, Mn, Fe, Ni, Cu, Mo, W, Nb, and Ta; $0.5 \leq m \leq 1.2$; $0 \leq n \leq 0.5$; $0.5 \leq p \leq 1.2$; $0 \leq q \leq 0.5$; and $2.7 \leq r \leq 3.3$; and

20 a complex oxide represented by the formula $(\text{Ln}_s\text{R}^3_t)_2\text{Ni}_u\text{R}^4_v\text{O}_w$ wherein Ln is one or more elements selected from the group consisting of lanthanoids; R^3 is one or more elements selected from the group consisting of Na, K, Sr, Ca, and Bi; R^4 is one or more elements selected from the group consisting of Ti, V, Cr, Mn, Fe, Ni, Cu, Mo, W, Nb, and Ta; $0.5 \leq s \leq 1.2$; $0 \leq t \leq 0.5$; $0.5 \leq u \leq 1.2$; $0 \leq v \leq 0.5$; and $3.6 \leq r \leq 4.4$; and

25 (ii) at least one powdery electrically conductive metal selected from the group consisting of gold, silver, platinum, and alloys containing at least one of these metals.

30 14. A thermoelectric element wherein one end of a p-type thermoelectric material and one end of an n-type thermoelectric material are each connected to an electrically conductive substrate with an electrically

conductive paste;

the p-type thermoelectric material comprising a complex oxide represented by the formula $Ca_aA^1_bCo_4O_e$ wherein A^1 is one or more elements selected from the group consisting of Na, K, Li, Ti, V, Cr,

5 Mn, Fe, Ni, Cu, Zn, Pb, Sr, Ba, Al, Bi, Y, and lanthanoids; $2.2 \leq a \leq 3.6$; $0 \leq b \leq 0.8$; and $8 \leq e \leq 10$; or a complex oxide represented by the formula $Bi_fPb_gM^1_hCo_2O_k$ wherein M^1 is one or more elements selected from the group consisting of Sr, Ca, and Ba; $1.8 \leq f \leq 2.2$; $0 \leq g \leq 0.4$; $1.8 \leq h \leq 2.2$; and $8 \leq k \leq 10$;

10 the n-type thermoelectric material comprising a complex oxide represented by the formula $La_mR^1_nNiO_r$ wherein R^1 is one or more elements selected from the group consisting of Na, K, Sr, Ca, and Bi;

$0.5 \leq m \leq 1.2$; $0 \leq n \leq 0.5$; and $2.7 \leq r \leq 3.3$; or a complex oxide represented by the formula $(La_sR^3_t)_2NiO_w$ wherein R^3 is one or more elements selected

15 from the group consisting of Na, K, Sr, Ca, and Bi; $0.5 \leq s \leq 1.2$; $0 \leq t \leq 0.5$; and $3.6 \leq w \leq 4.4$;

the electrically conductive paste for connecting the p-type thermoelectric material to the electrically conductive substrate comprising (i) at least one powdery oxide selected from the group

20 consisting of a complex oxide represented by the formula $Ca_aA^1_bCo_4O_e$ wherein A^1 is one or more elements selected from the group consisting of Na, K, Li, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Pb, Sr, Ba, Al, Bi, Y, and lanthanoids; $2.2 \leq a \leq 3.6$; $0 \leq b \leq 0.8$; and $8 \leq e \leq 10$; and a complex oxide represented by the formula $Bi_fPb_gM^1_hCo_2O_k$ wherein M^1 is one or more

25 elements selected from the group consisting of Sr, Ca, and Ba; $1.8 \leq f \leq 2.2$; $0 \leq g \leq 0.4$; $1.8 \leq h \leq 2.2$; and $8 \leq k \leq 10$; and (ii) at least one powdery electrically conductive metal selected from the group consisting of gold, silver, platinum, and alloys containing at least one of these metals; and

30 the electrically conductive paste for connecting the n-type thermoelectric material to the electrically conductive substrate comprising (i) at least one powdery oxide selected from the group consisting of a complex oxide represented by the formula $La_mR^1_nNiO_r$ wherein R^1 is one or more elements selected from the group consisting

35 of Na, K, Sr, Ca, and Bi; $0.5 \leq m \leq 1.2$; $0 \leq n \leq 0.5$; and $2.7 \leq r \leq$

3.3; and a complex oxide represented by the formula $(La_sR^3_t)_2NiO_w$ wherein R³ is one or more elements selected from the group consisting of Na, K, Sr, Ca, and Bi: 0.5 ≤ s ≤ 1.2; 0 ≤ t ≤ 0.5; and 3.6 ≤ w ≤ 4.4; and (ii) at least one powdery electrically conductive metal selected from 5 the group consisting of gold, silver, platinum, and alloys containing at least one of these metals.

15. A thermoelectric module comprising a plurality of the thermoelectric elements of Claim 12, wherein the thermoelectric elements are connected in series such that an unbonded end portion 10 of the p-type thermoelectric material of one thermoelectric element is connected to an unbonded end portion of the n-type thermoelectric material of another thermoelectric element on a substrate.

15 16. A thermoelectric conversion method comprising positioning one side of the thermoelectric module of Claim 15 at a high-temperature environment and positioning the other side of the module at a low-temperature environment.

20 17. A thermoelectric module comprising a plurality of the thermoelectric elements of Claim 13, wherein the thermoelectric elements are connected in series such that an unbonded end portion 25 of a p-type thermoelectric material of one thermoelectric element is connected to an unbonded end portion of an n-type thermoelectric material of another thermoelectric element on a substrate.

30 18. A thermoelectric conversion method comprising positioning one side of the thermoelectric module of Claim 17 at a high-temperature environment and positioning the other side of the module at a low-temperature environment.